

Phenols From Pyrolysis Of Tobacco Leaf Acids

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In view of current interest (1,2,9) in the origin of the simple phenols present in cigarette smoke (3,6,11, 12), we wish to report our preliminary findings on the pyrolytic formation of such phenols from malic, citric and other acids. Malic and citric acids are reported to comprise about 10 and 0.6%, respectively, of the dry weight of flue-cured leaf (4).

Individual acids were pyrolyzed at 700°C in either quartz or vycor tubes continually flushed with nitrogen (30 ml/min). Products were collected in a series of glass traps progressively cooled in ice-water and Dry Ice-acetone, and fractionated in the usual way to remove phenols (8,12).

Gas liquid chromatographic (GLC) examination of the phenolic products, under conditions described (8, 12), indicated the presence of phenol, o-cresol, and m- and/or p-cresol in the pyrolysates of malic, citric and other acids (Table). Meta- and para-cresol were not resolvable by GLC. Thin-layer chromatographic studies, following reaction of the phenols with diazotized p-nitroaniline (10), substantiated the GLC findings.

Cis-aconitic acid, although not re-

Levels of phenols from the pyrolysis of certain acids (in mg/100 g pyrolyzed).

Acid pyrolyzed (700°C, N ₂)	Phenols		
	Phenol	o-Cresol	m- and p-Cresol
Malic*	8.9	7.9	7.9
Citric*	2.5	3.8	5.1
Cis-aconitic	8.5	12	22
Fumaric*	1.0	0.7	0.3
Sodium Citrate*	1.0	3.0	1.5
Sodium Lactate*	41	25	25

* Reportedly present in tobacco (7).

ported as present in cured leaf, is structurally related to citric acid and was pyrolyzed to gain insight into the mechanism of the pyrolytic reaction. The levels of phenols in the pyrolysates were estimated by measurement of GLC peak areas (subject to limitations of the isolation procedure) and were generally low (Table). For a reason as yet obscure, sodium lactate gave relatively high yields of phenols on pyrolysis. The reaction mechanisms of these

acid-to-phenol conversions lend themselves to much conjecture. The observation that both citric and cis-aconitic acid give rise to phenols in much the same qualitative, if not quantitative, pattern suggests a common pyrolytic pathway for the two acids. It suggests also that the β -hydroxyl group of citric acid is not essential for phenol formation, and that the phenolic oxygen probably arises from another source (e.g. the carboxyl groups).

Both citric and cis-aconitic acids can ostensibly give rise to three-carbon fragments by appropriate decarboxylation reactions; two such C_3 fragments can, in turn, condense to form a benzene nucleus, or undergo further fragmentation to yield methyl groups (for cresol formation). Reasoning similar to the above can be used to propose pathways through which the other acids might give rise to phenols via pyrolysis. Gilbert and Lindsey have shown previously that pyrolysis of citric, malic and oxalic acids leads to the formation of small amounts of polynuclear aromatic hydrocarbons (5).

The foregoing data show that citric, malic and related acids give rise to phenols on pyrolysis. The yields, however, are lower than those from other phenol-forming materials present in tobacco leaf (1,2,9). This observation suggests that individually these acids contribute little to the overall phenol content of cigarette smoke, although their cumulative effect may be more significant. The data do, however, lend credence to the notion that many type of materials may serve as potential phenol precursors through many diverse pathways (9).

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